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SUBJECT: PRELIMINARY MONITORING RESULTS OF THE THIRD AND FOURTH SPINOSAD AERIAL APPLICATIONS FOR MEXICAN FRUIT FLY ERADICATION IN VALLEY CENTER, SAN DIEGO COUNTY (STUDY 216)

The Department of Pesticide Regulation (DPR) conducted monitoring for the third and fourth in a series of spinosad aerial applications to eradicate the Mexican fruit fly in San Diego County, California on February 4-5, 2003, and February 18-19, 2003. During these applications, DPR staff collected deposition, surface water, air, fruit, and tank samples. In addition, run-off water samples were collected during a storm event at two sites on Keys Creek. Deposition samples were taken at 23 sites with average concentrations of 2.08 and 2.12 µg/ft^2 (0.091 and 0.092 grams per acre [g/ac]) for the third and fourth applications, respectively. These achieved 64% and 65% of the 3.26 µg/ft^2 (0.14 g/ac, or 35.1 µg/m^2) target application rate and 15% higher than the first two applications. Deposition samples were also collected at three sites within the Keys Creek buffer zone. Spinosad was detected in two of three samples during the third application at 0.14 and 0.19 µg/ft^2 and in one sample during the fourth application at 0.31 µg/ft^2. None of the surface water, run-off water, and air samples contained detectable residues of spinosad. One of the four background fruit samples contained a trace amount of residue in both third and fourth applications. Fruit samples collected after the applications contained 0.004-0.034 parts per billion (ppb) (ng/g) spinosad residue for the third application and 0.007-0.0162 ppb for the fourth application. Tank mix concentrations for the third and fourth applications were 0.0096% and 0.0080%, respectively, versus a target concentration of 0.0080%. Analysis of the tank mix for organophosphates showed 5 parts per million (ppm) and 290 ppm malathion for the third and fourth applications, respectively. No carbamates or chlorinated hydrocarbons were detected.

Introduction

The California Department of Food and Agriculture (CDFA) is conducting aerial applications with spinosad to eradicate the Mexican fruit fly infestation in the Valley Center area of San Diego County. The application area consists of 28 square miles (mi^2), of which 23 mi^2

is treated using aerial applications and five square miles is treated using ground applications. CDFA plans to aerially apply spinosad every two weeks for two life cycles of the pest to effectuate eradication.

Materials and Methods

The pesticide product and application method used in these applications were the same as the previous applications, using GF-120 NF Naturalyte Fruit Fly Bait (U.S. Environmental Protection Agency Registration Number 62719-498), containing 0.020% spinosad by weight (mixture of spinosyn A and spinosyn D) as the active ingredient. For application, the GF-120 NF was diluted with water to a tank mix target concentration of 0.0080% by weight of spinosad or 0.363 grams per gallon (g/gal). The spinosad (active ingredient) target application rate was 3.26 $\mu g/ft^2$ (0.142 g/acre, or 35.1 $\mu g/m^2$). The third application started on February 4 at 8:05 p.m. and ended on February 5 at 5:04 a.m. The fourth application started on February 18 at 8:00 p.m. and ended on February 19 at 5:08 a.m. The applications were made using three fixed-wing aircraft, each with a swath width of 100 feet (ft), sprayed in east and west directions at an altitude of approximately 500 ft. CDFA established buffer zones around several water bodies and excluded them from the aerial application.

Spinosad residues were measured in deposition, surface water, run-off water, air, fruit, and spray tank mixture samples. Deposition samples were collected using one ft^2 mass deposition sheets. Deposition sheets were set at 23 sampling sites dispersed throughout the treatment area (Figure 1). In addition, three deposition sites were sampled within the buffer zone around Keys Creek. The sheets were set at sampling sites before application and collected after each application.

Background water samples were collected from Keys Creek (Figure 1) before application on February 4 and 18 and water samples were also collected after application on February 5 and 19, for the third and fourth application, respectively. Since it rained early morning on February 20 (day after the fourth application), additional water samples were collected. However, it is unlikely any run-off developed due to the small amount of rain that fell, approximately 0.04 inches. These samples were designated as post-application.

Seventeen run-off water samples were collected on February 11 after rain at one site and on February 12 during rain at two sites on Keys Creek (Figure 2). One site is at mid-stream within the treatment area and is used for the surface water sampling. Twelve samples were taken at this site approximately every 1.5 hours on February 11 and every hour on February 12. The other site is downstream, approximately five miles outside the treatment area. Five samples were taken at this site, approximately every hour from 1:00 p.m. to 5:00 p.m. on February 12. On February 11, it started raining at 5:00 a.m. and stopped at 2:00 p.m., accumulating 0.57 inches

precipitation. On February 12, there were scattered showers for less than an hour approximately from 12:30 a.m. to 1:30 a.m. and steady rain for 8 hours from 9:00 a.m. to 5:00 p.m., accumulating 0.84 inches precipitation in Valley Center.

Air samples were collected from four sites (Figure 1) using XAD-2/glass-fiber filter tubes (SKC#226-30-16) and personal air sampling pumps (SKC#224-PCXR8) at a constant flow rate of approximately 3000 ml/min. At each of the four sites, a single sampler was set approximately four to six feet above the ground and protected from direct application. Background air samples were taken for approximately 24 hours before application; application samples were collected for the duration of application; and post-application samples were taken for 24 hours after application.

Fruit samples were collected from two orchards (Figure 1). At each sampling site, two grapefruit trees were randomly picked (the same trees are being used for the duration of the treatment program) and two samples were collected, one from the upper and the other from the lower portions of the trees at randomly chosen compass direction. For each sample, two grapefruit were collected from each tree and were composited into one sample, placed into a stainless steel bucket, and covered with a stainless steel lid. Background fruit samples were collected prior to application and application samples were collected 4-5 hours after application.

Deposition, air, fruit, and duplicate surface water samples were stored on dry ice; surface water, run-off water, and tank mix samples were stored on ice until delivery to the CDFA Center for Analytical Chemistry for analysis. All samples were analyzed for spinosyns A and D, as well as spinosyn B, a breakdown product. The deposition samples were extracted with methanol and analyzed using a liquid chromatograph with a tandem mass spectrometer detector (LC/MS/MS), providing a quantitation limit of 0.1 µg/ft^2. The water samples were extracted with methylene chloride and analyzed using LC/MS/MS, providing a quantitation limit of 0.05 (ppb). Air samples were extracted with methanol and methylene chloride, and analyzed using LC/MS/MS providing a quantitation limit of 0.5 µg/sample (0.116 µg/m^3). Grapefruit samples were extracted with acetonitrile and water, and analyzed using LC/MS/MS providing a quantitation limit of 1 ppb. Outer-surface of fruit and inner surface of sample containers were rinsed with methanol and analyzed using LC/MS/MS providing a quantitation limit of approximately 0.0024 ppb (ng/g) fruit basis. The tank mix sample was extracted with acetone and analyzed using a high-performance liquid chromatograph and ultraviolet detector, providing a quantitation limit of one ppm (0.0001%). The tank mixture sample was also screened for organophosphates, carbamates, and chlorinated hydrocarbons.

Results

Results of the deposition samples are listed in Table 1. All 23 deposition samples had a detectable amount of spinosad, ranging from 0.58 to 4.46 µg/ft^2 and from 0.05 to 9.63 µg/ft^2 for the third and fourth application, respectively. Average concentrations of the third and fourth applications were 2.08 µg/ft^2 and 2.12 µg/ft^2, respectively, and achieved 64% and 65% of the 3.26 µg/ft^2 target application rate. These results are 15% higher than the first two applications (Figure 3).

Two of the three buffer zone deposition samples detected 0.14 and 0.19 µg/ft^2 of spinosad in the third application. One of these two sites also had concentration of 0.31 µg/ft^2 in the fourth application (Table 2). These results were similar to the average of the first two applications.

Spinosad was not detected in any of the surface water, run-off water, and air samples. These results were the same as the first two applications.

Background fruit samples collected from the upper portion of the sampling trees at one orchard contained trace amount of spinosad for both the third and fourth applications. All other background samples had no detectable spinosad residues. All fruit samples collected after application contained measurable amounts of spinosad for both the third and fourth applications. Dividing the amount of spinosad detected by the fruit sample weight, gives concentrations ranging from 0.004 to 0.034 ppb for the third application and from 0.007 to 0.162 ppb for the fourth application (Table 3). The grapefruit samples collected for these applications were not mature and, therefore, are unsuitable for determining legal compliance with the tolerance. All application samples were less than the 300 ppb tolerance level. Spinosad residues for these applications were higher than those in the second application partially due to a change in the method of rinsing samples. Only the sample container was rinsed in the second application and both fruit and container were rinsed for the third and fourth applications.

Spinosad concentrations for the tank mix samples were 0.0096% and 0.0080% for the third and fourth application, respectively (Table 4). These concentrations were 120% and 100% of the nominal target concentration, 0.0080%. In the third and fourth application, 5872 and 5802 gallons, respectively, of spinosad mix was applied over 14,847 acres. If the tank mixes contained the target concentration, the actual application rates for the third and fourth application would be, respectively, 3.30 and 3.26 µg/ft^2 (i.e. 101% and 100% of the target rate [3.26 µg/ft^2, 0.14 g/ac, or 35.1 µg/m^2]), compared to 91% and 96% in the first and second application, respectively. Organophosphate screening indicated 5 ppm and 290 ppm malathion in the samples collected for the third and fourth application, respectively. Malathion was not detected in the first two applications. No carbamate or chlorinated hydrocarbon pesticides screened were detected. Follow-up sampling of the mix/load system for malathion will be described in a separate report.

The third application occurred during a clear night with temperature 32-42º F, relative humidity 56-76%, and wind speed 0-1 miles per hour (mph). The fourth application was conducted three days after rain, in a clear night with temperature 37-48º F, relative humidity 99%, and wind speed 2-4 mph.

Results reported here are also available at DPR's Web site at <http://www.cdpr.ca.gov/docs/mexfly/>.

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Table 1. Monitoring results for deposition samples. The amount of spinosad is sum of the individual spinosyns (A, D, and B). The target amount is 3.26 µg/ft^2.

Site Code	Spinosad (µg/ft^2)	
	Third Application	**Fourth Application**
	February 4-5, 2003	February18-19, 2003
1	1.962[a]	0.054
2	1.145	1.502
3	0.809	0.736
4	1.205	0.937
5	3.229	0.563
6	2.559	0.934
7	1.133	2.084
8	1.259	9.631
9	4.413	4.051
10	3.420	2.405
11	1.910	2.402
13	1.094	0.498
14	1.140	8.367
15	1.236	1.477
16	4.155	3.603
17	1.687	2.959
18	3.200	0.794
19	4.681	1.314
20	1.235	0.118
22	1.622	2.656
23	0.584	0.522
25	3.009	0.413
26	1.169	0.740
Average	**2.081**	**2.120**
Std. Dev.	**1.235**	**2.442**
Minimum	**0.584**	**0.054**
Maximum	**4.681**	**9.631**

[a] Sum of detected spinosyns (A, D, and B), wherever none detected the quantity of 0 µg/ft^2 was used and wherever trace amount (less than the quantitation limit 0.1 µg/ft^2 for each individual spinosyn A, D, and B**)** was detected, the quantity of (quantitation limit + detection limit)/2 µg/ft^2 was used to calculate the sum of spinosyns in this report.

Table 2. Monitoring results for buffer zone deposition samples. The amount of spinosad is sum of the individual spinosyns (A, D, and B).

Site Code	Spinosad (µg/ft^2)	
	Third application	**Fourth Application**
	February 4-5, 2003	February 18-19, 2003
12	ND[a]	ND
21	0.186[b]	0.312
24	0.140	ND

[a] None Detected, with a detection limit of 0.008, 0.020, and 0.028 µg/ft^2 for spinosyn A, D, and B, respectively.

[b] Sum of detected spinosyns (A, D, and B), wherever none detected the quantity of 0 µg/ft^2 was used and wherever trace amount (less than the quantitation limit 0.1 µg/ft^2 for each individual spinosyn A, D, and B**)** was detected, the quantity of (quantitation limit + detection limit)/2 µg/ft^2 was used to calculate the sum of spinosyns in this report.

Table 3. Monitoring results for fruit samples. The total spinosad is sum of spinosyns (A, D, and B) in both fruit and rinse of fruit and container.

		Spinosad (ppb)			
Site	**Sampling**	**Third application**		**Fourth Application**	
Code	**Portion**	**Background**	**Application**	**Background**	**Application**
3	upper	0.001[a]	0.004	0.001	0.149
3	lower	ND[b]	0.023	ND	0.162
27	upper	ND	0.034	ND	0.007
27	lower	ND	0.023	ND	0.011

[a] Sum of detected spinosyns (A, D, and B) in fruit and rinse of fruit and container, wherever trace amount was detected in the rinse, the quantity of half quantitation limit was used to calculate the sum in this report.

[b] None Detected, with a detection limit for fruit samples at 0.903, 0.716, and 0.959 ppb spinosyn A, D, and B, respectively, and a quantitation limit for rinse of fruit and container at 3 ng/sample (~0.0024 ppb). Detection limit for rinse was not available.

Table 4. Monitoring results for tank samples. The amount of total spinosad is sum of the individual spinosyns (A, D, and B). The target tank mix concentration is 0.008%.

	Application	
	Third	**Fourth**
Spinosad (%)	0.0096	0.0080
% of Target	120	100

Figure 1. Sampling sites for the third and fourth aerial spinosad applications
(February 4-5 and February 18-19, 2003)

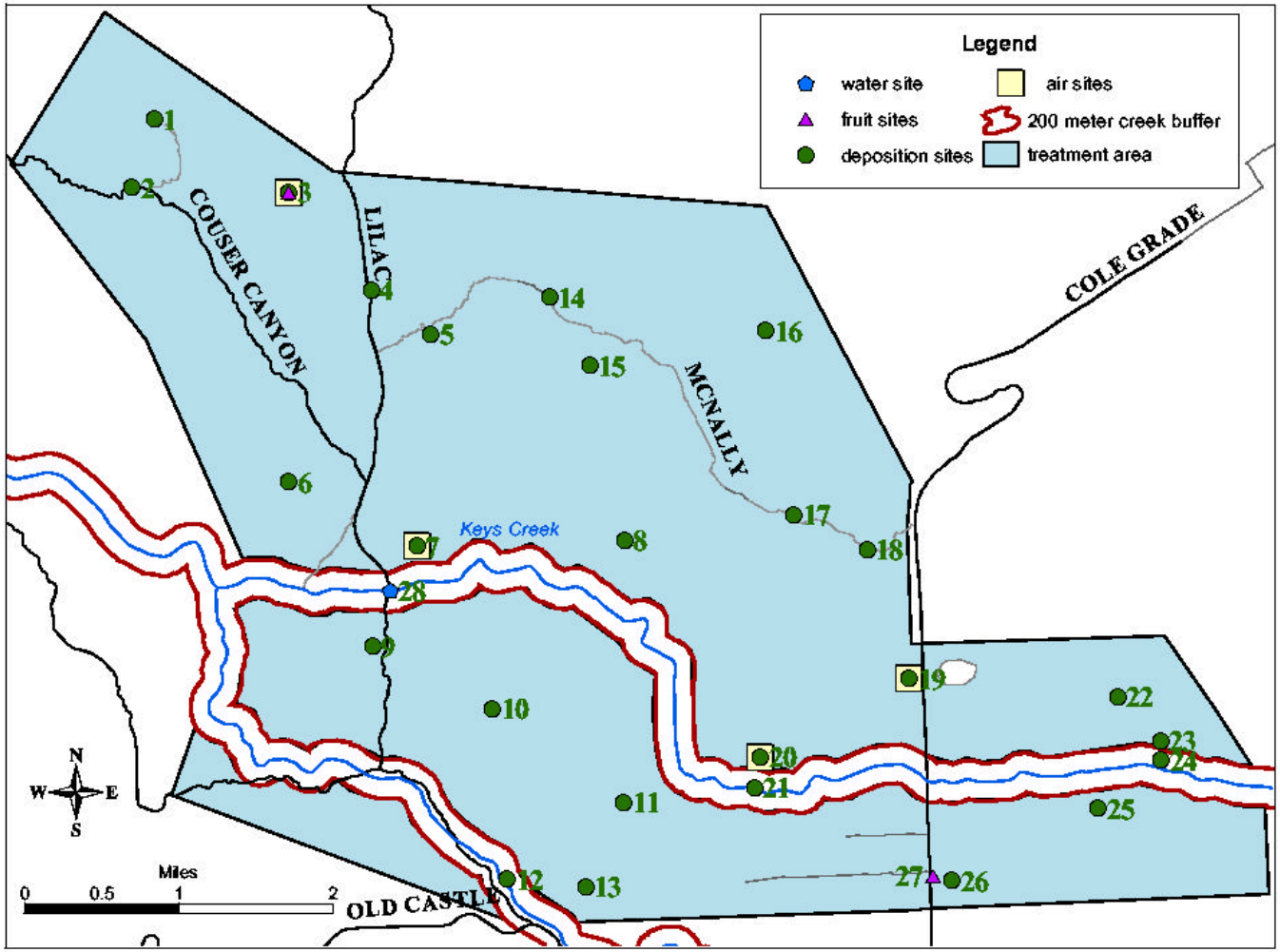

Figure 2. Sampling sites for run-off water (February 11-12, 2003)

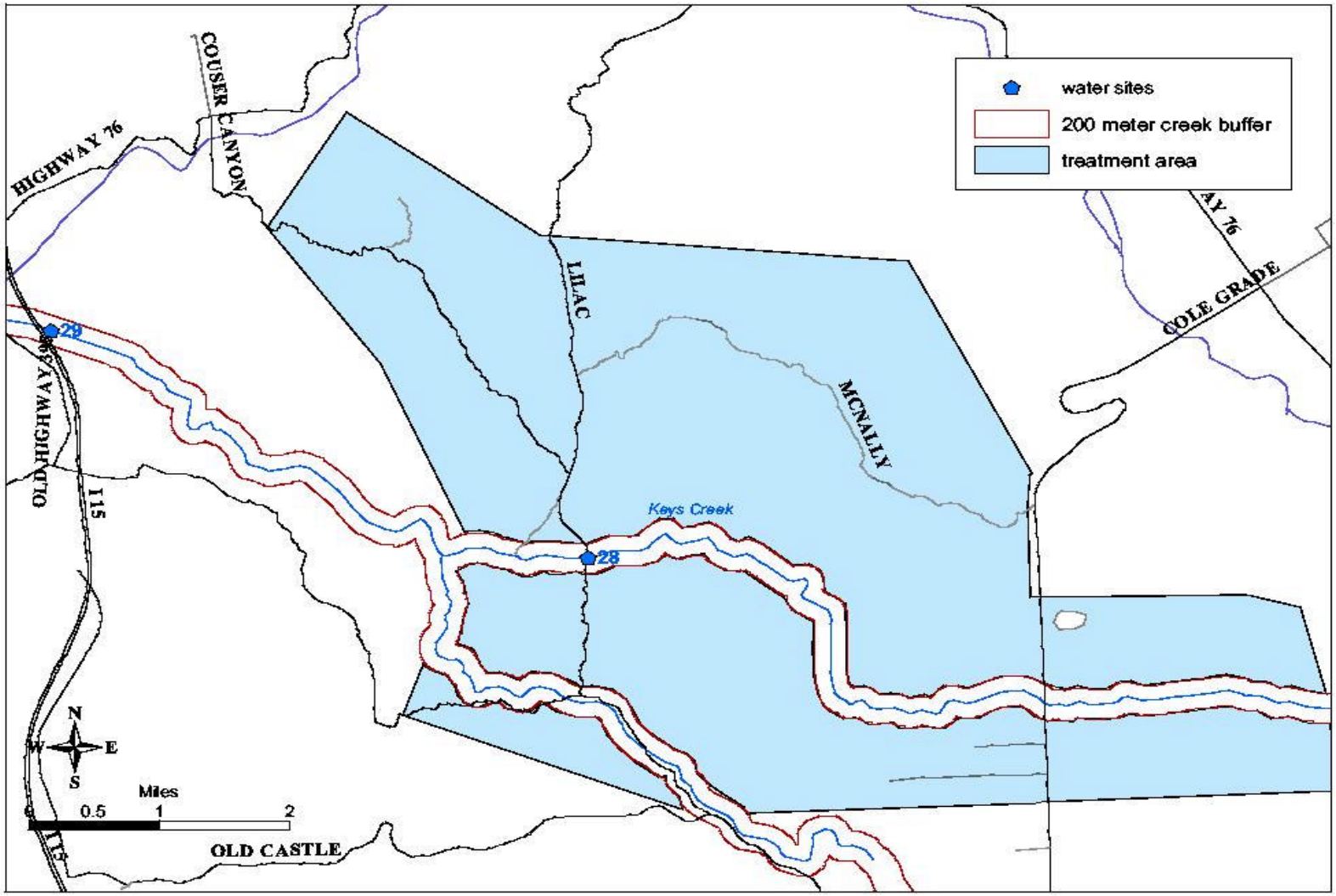

Figure 3. Comparison of average (± 1 standard error) deposition spinosad.